

# B.Sc. Semester – I

## Subject: - CHE - 101: Catalysis and Adsorption

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### ➤ Contents:

#### ✓ **Catalysis**

- Definition of catalyst and catalysis
- Types of catalyst: positive catalyst, negative catalyst and auto catalyst
- Catalytic reaction: Homogeneous catalytic reaction and Heterogeneous catalytic reaction
- Characteristics of catalyst
- Action of finely divided catalyst
- Catalytic promoters or activators
- Catalytic poisons or anticatalysts
- Enzyme catalyst: definition and characterization

#### ✓ **Adsorption**

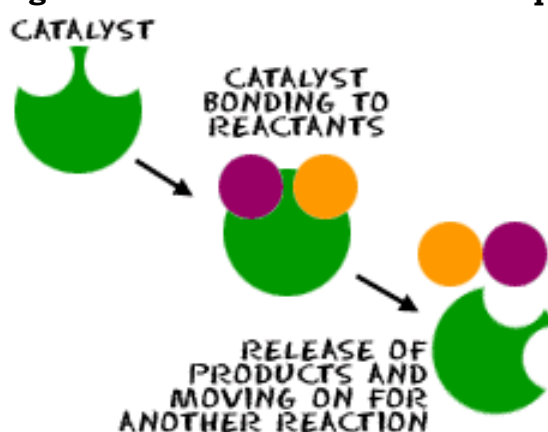
- Definition of adsorption, absorption, positive adsorption, negative adsorption, adsorbate, desorption
  - Types of adsorption (physical adsorption chemical adsorption)
  - Adsorption gases by solids
  - Freundlich and Langmuir adsorption isotherm (derivation)
  - Application of adsorption
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### **Introduction**

**Jöns Jakob Berzelius** (1836) realized that, there are substances which, **increases rate** of a reaction **without** themselves being **consumed**. He believed that function of such a substance was to loosen the bonds which hold the atoms in the reacting molecules together. Thus he coined the term Catalysis (Greek-Kata = wholly, Lein = to loosen).

There is no doubt, that usually a catalyst accelerates a reaction as was originally thought by Berzelius. But A number of cases are now known where the catalyst definitely retards (slows down) the rate-of n reaction.

**Catalyst** is defined as a **substance**, which **alters the rate of** a chemical **reaction**, itself remaining **chemically unchanged** at the end of the reaction. The **process** is called **Catalysis**.



As evident from the above definition, a catalyst may increase or decrease the rate of a reaction.

A catalyst which **enhances** the rate of a reaction is called a **Positive Catalyst** and the process Positive Catalysis or simply Catalysis.

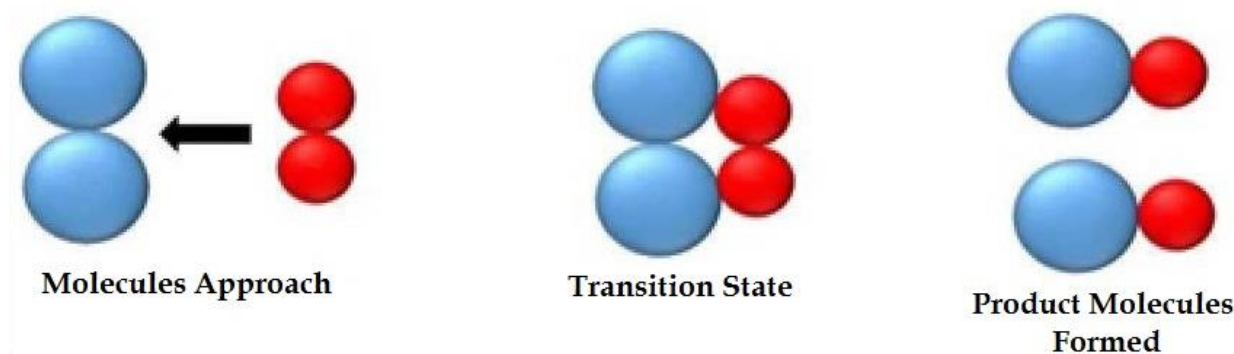
A catalyst which **retards** the rate of a reaction is called a **Negative Catalyst** or **inhibitors** and the process Negative Catalysis.

### **Mechanism of Catalysis**

Catalysts work by changing the activation energy for a reaction, i.e., the minimum energy needed for the reaction to occur. This is accomplished by providing a new mechanism or reaction path through which the reaction can proceed. When the new reaction path has a lower activation energy, the reaction rate is increased and the reaction is said to be catalyzed.

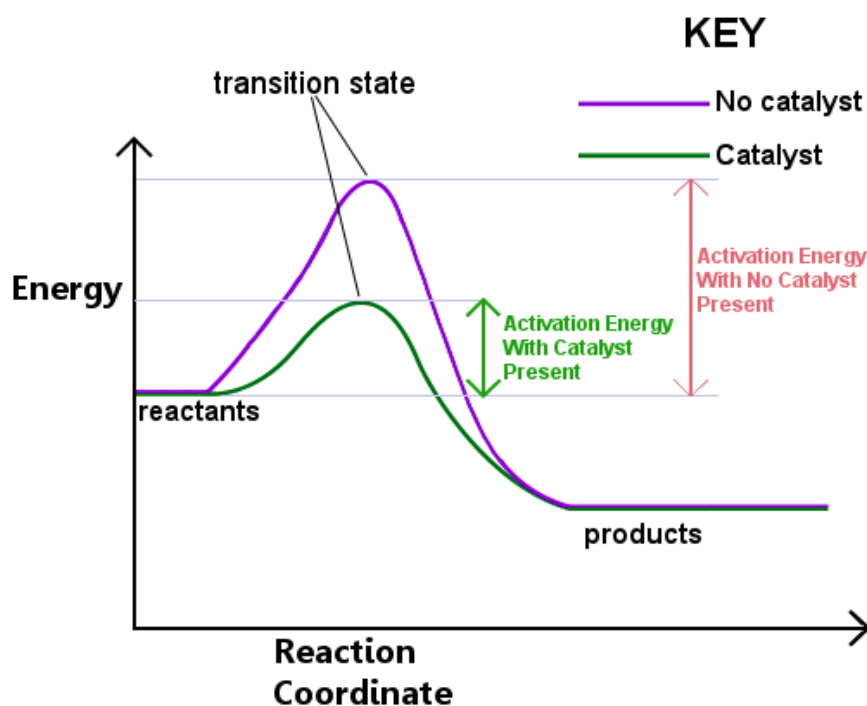
## Activation Energy and Catalysis

According to the collision theory, a reaction occurs by the collisions between the reactant molecules (or ions).



At ordinary temperature, the molecules do not possess enough energy and hence the collisions are not effective. However, when the temperature of the system is raised, the kinetic energy of the molecules increases. But the molecules do not react unless they attain a minimum amount of energy. **The minimum amount of energy required to cause a chemical reaction is known as the Activation energy.** The Activation Energy ( $E_a$ ) determines how fast a reaction occurs, the higher Activation barrier, the slower the reaction rate, the lower the Activation barrier, the faster the reaction. The activated molecules on collision first form an Activated Complex. As a result of breaking and forming of new bonds, the activated complex dissociates to yield product molecules.

When a catalyst is present, it lowers the activation energy of the reaction by providing a new pathway (mechanism). Thus larger numbers of effective collisions occur in the presence of the catalyst than would occur at the same temperature without the presence of the catalyst. In this way, the presence of the catalyst makes the reaction go faster, other conditions remaining the same.



Energy diagram of reaction with and without catalyst, showing clearly lowering of activation energy by catalyst

### Types of Catalyst

#### There are two main types of Catalyst

- ✓ Homogeneous Catalyst
- ✓ Heterogeneous Catalyst

#### Some other Types of Catalyst

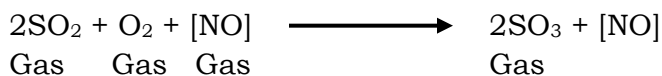
- ✓ Positive Catalyst
- ✓ Negative Catalyst
- ✓ Auto Catalyst
- ✓ Acid-Base Catalyst
- ✓ Enzyme Catalyst

## Homogeneous catalysis

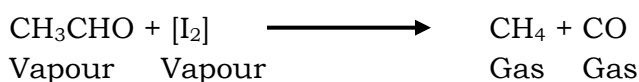
In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) phase.

### 1. Examples of homogeneous catalysis in gas phase

- a. Oxidation of sulfur dioxide (SO<sub>2</sub>) to sulfur trioxide (SO<sub>3</sub>) with nitric oxide (NO) as catalyst



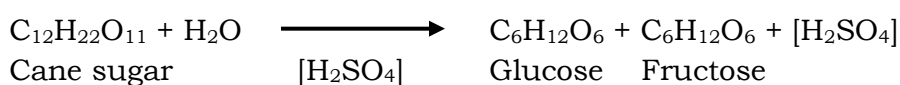
- b. Decomposition of Acetaldehyde (CH<sub>3</sub>CHO) with iodine (I<sub>2</sub>) as catalyst



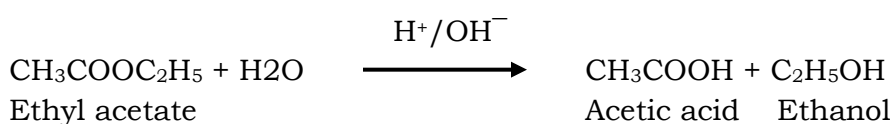
### 2. Examples of homogeneous catalysis in solution phase

Many reactions in solutions are catalyzed by acids (H<sup>+</sup>) and bases (OH<sup>-</sup>)

- a. Hydrolysis of cane-sugar in aqueous solution in presence of mineral acid as catalyst



- b. Hydrolysis of an ester in the presence of acid or alkali,



## Heterogeneous catalysis

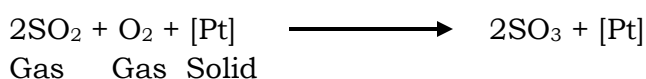
The Catalysis, in which the catalyst is in a different physical phase from the reactant, is termed Heterogeneous catalysis. The most important of such reactions are those in which the reactants are in the gas phase, while the catalyst is a solid. The process is called Contact catalysis since the reaction occurs by contact of reactants with the catalyst surface. In contact catalysis, usually the catalyst is a finely divided metal or gauze. This form of catalysis has great industrial importance.

### Examples of Heterogeneous Catalysis

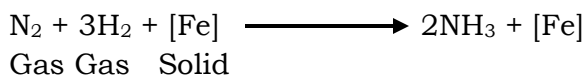
Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are listed below.

#### 1. Heterogeneous catalysis with gaseous reactants (Contact catalysis)

- a. Combination of sulfur dioxide (SO<sub>2</sub>) and oxygen in the presence of finely divided platinum or vanadium pentoxide V<sub>2</sub>O<sub>5</sub> (contact process for sulfuric acid)

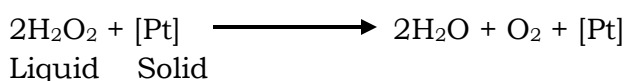


- b. Combination of Nitrogen and Hydrogen to form ammonia in the presence of finely divided iron, [Haber process for ammonia]

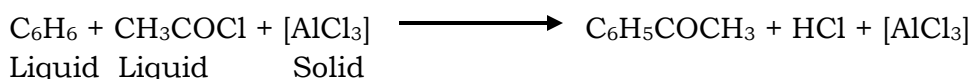


#### 2. Heterogeneous catalysis with liquid reactants

- a. The decomposition of aqueous solutions of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is catalyzed by manganese dioxide (MnO<sub>2</sub>) or platinum in colloidal form.

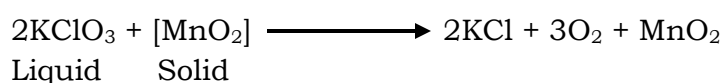


- b. Benzene and ethenoyl chloride (CH<sub>3</sub>COCl) react in the presence of anhydrous aluminum chloride to form phenyl methyl ketone (C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>)



#### 3. Heterogeneous catalysis with Solid reactant

The decomposition of potassium chlorate (KClO<sub>3</sub>) is catalyzed by manganese dioxide (MnO<sub>2</sub>)



## Positive catalysis

Catalysts that speed the reaction are called positive catalysts. A positive catalyst lowers the activation energy, increases the reaction rate.

Example:

1. In Haber's process for the synthesis of ammonia, iron which acts as a catalyst.



2. The decomposition of aqueous solutions of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is catalyzed by platinum

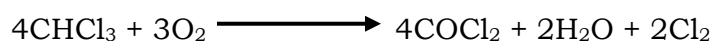


## Negative catalysis (Inhibitor)

When a catalyst reduces the rate of a reaction, it is called a Negative catalyst or Inhibitor. This phenomenon is called Negative catalysis or Inhibition. Negative catalysis is useful to slow down or stop altogether an unwanted reaction.

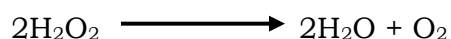
Example:

1. Oxidation of trichloromethane ( $\text{CHCl}_3$ ). Trichloromethane (or chloroform) is used as an anesthetic upon oxidation by air, it forms carbonyl chloride ( $\text{COCl}_2$ ) which is a poisonous substance.



2% of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) when added to chloroform acts as a negative catalyst and suppresses the formation of carbonyl chloride.

2. Decomposition of Hydrogen peroxide. The decomposition of hydrogen peroxide is retarded by the presence of dilute acids or glycerol.



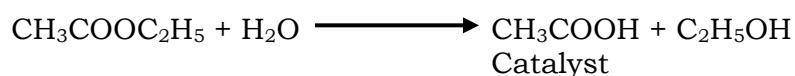
## Auto catalysis

When one of the products of a reaction itself acts as a catalyst for that reaction the phenomenon is called auto-catalysis. In auto-catalysis, the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily.

Examples:

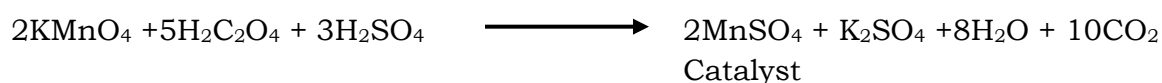
1. Hydrolysis of an ester

The hydrolysis of ethyl acetate forms acetic acid ( $\text{CH}_3\text{COOH}$ ) and ethanol. Of these products acetic acid acts as a catalyst for the reaction.



2. Oxidation of oxalic acid

When oxalic acid is oxidized by acidified potassium permanganate, manganese sulfate produced during the reaction acts as catalyst for the reaction.



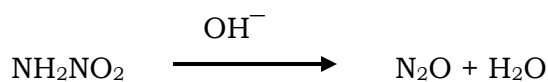
## Acid Base catalysis

A number of homogeneous catalytic reactions are known which are catalyzed by acids or bases or both acids and bases. These are often referred to as Acid-Base Catalysts.

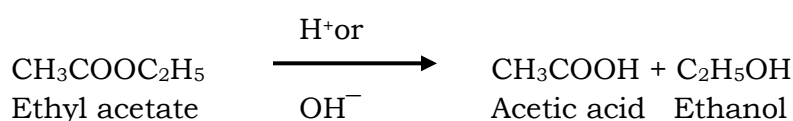
Arrhenius pointed out that acid catalysis was, in fact, brought about by  $\text{H}^+$  ions supplied by strong acids, while base catalysis was caused by  $\text{OH}^-$  ions supplied by strong bases.

Examples:

1. Decomposition of nitramide



2. Hydrolysis of an Ester



## Enzyme catalysis

This will be discussed separately at a later stage.

## Characteristic of Catalyst

Although there are different types of catalytic reactions, the following features or characteristic, are common to most of them. These features are often referred to as the criteria of catalysis

### 1. A catalyst remains unchanged in mass and chemical composition at the end of reaction

Qualitative and Quantitative analysis shows that catalyst undergoes no change in mass or chemical nature however; it may undergo a physical-change. Thus, granular manganese dioxide ( $\text{MnO}_2$ ) used as catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.

### 2. A small quantity of catalyst is generally needed to produce almost unlimited reaction

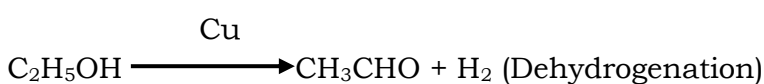
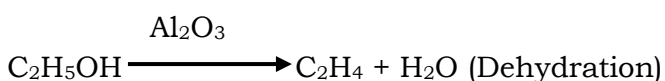
Sometimes a trace of a metal catalyst is required to affect very large, amount of reactant, For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyze the decomposition of hydrogen peroxide.

### 3. A catalyst is more effective when finely divided

In heterogeneous catalysis the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinized asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

### 4. A catalyst is specific in its action

While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) gives ethane ( $\text{C}_2\text{H}_6$ ) when passed over hot aluminum oxide, but with hot copper it gives ethanal ( $\text{CH}_3\text{CHO}$ )



### 5. A catalyst in general, cannot initiate a reaction

In most cases, a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction.

### 6. A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium

It implies that in a reversible reaction the catalyst accelerate the forward and reverse reaction equally. Thus the ratio of the rates of two opposing reaction i.e. equilibrium constant, remains unchanged

### 7. Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst

We have already studied the effect of temperature change on reversible reactions under Le Chatelier Principle. Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise in the temperature may cause their coagulation. In such a case, the rate of reaction increases up to a certain point and then gradually decreases. The rate of reaction is maximum at a particular temperature; the Optimum temperature.

## Homogeneous catalytic reaction and Heterogeneous catalytic reaction

### 1. Phase

#### a. Homogeneous: Liquid.

When a reactant is in the gas form such as in hydrogenation, what reacts is actually the gas dissolved in the liquid phase, and not the one in the gas phase.

#### b. Heterogeneous: Liquid, Gas, Solid

### 2. Operative Temperature

#### a. Homogeneous: Generally low temperatures.

The presence of a solvent, which needs to dissolve the catalyst, might limit the temperature of the reaction.

#### b. Heterogeneous: The only limitation is the stability of the catalyst under harsh conditions.

### 3. Diffusivity

- a. Homogeneous: High diffusivity. Having all reactants and catalyst in one phase enhances dramatically the diffusivity under proper stirring.
- b. Heterogeneous: Diffusivity might be an issue for catalysts with low surface area.

### 4. Heat Transfer

- a. Homogeneous: High Heat Transfer. Having all reactants and catalyst in one phase enhances dramatically the heat transfer under proper stirring.
- b. Heterogeneous: Heat Transfer might be an issue due to the different heat capacities of reactants and catalyst.

### 5. Catalyst Separation

- a. Homogeneous: The separation of the products from the catalyst is generally expensive, the only exception being in biphasic catalysis.
- b. Heterogeneous: The separation of the products from the catalyst is usually straightforward.

### 6. Recycling

- a. Homogeneous: Recycling is expensive due to difficult treatment of the spent catalyst.
- b. Heterogeneous: Recycling is usually straightforward, although the catalyst might need reactivating treatment.

### 7. Active site

- a. Homogeneous: Usually well-defined. Catalysts are generally single atom transition metal stabilized by ligands.
- b. Heterogeneous: Mainly not well-defined. When dealing with metal particles on a support, the active site might be only a few percent of the metal (usually small particles), and different zones of the same particle might have different catalytic properties.

### 8. Catalyst modification

- a. Homogeneous: Relatively easy. Tuning of the electronic and steric properties on the metal can be done by varying donor atoms in the ligands or by tuning the donating abilities of the ligands.
- b. Heterogeneous: Relatively difficult. Control of the particle size and of the active site in general at the molecular level is extremely difficult. Few synthetic methods are available.

### 9. Reaction Mechanism

- a. Homogeneous: Easier to find out due to more techniques available. Direct methods are available.
- b. Heterogeneous: Difficult to find out. Mainly by indirect methods.

### 10. Selectivity

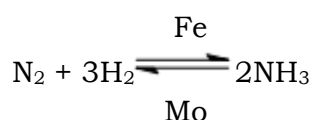
- a. Homogeneous: High. It is a consequence of the easier fine-tuning of the steric and electronic properties of the catalyst and of the easier way of finding out the reaction mechanism.
- b. Heterogeneous: Low. It is a consequence of more difficult fine-tuning of the steric and electronic properties of the catalyst and of the more difficult way of finding out the reaction mechanism.

## Promoters of Catalysis (Activators)

The activity of a catalyst can often be increased by addition of in small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble-catalyst. **A substance, which though itself not a catalyst, promotes the activity of a catalyst, is called a promoter.**

### Example:

Molybdenum (Mo) or aluminum oxide ( $\text{Al}_2\text{O}_3$ ) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.





## Characteristics of enzyme catalysis

In general, **enzymes** behave like **inorganic heterogeneous catalysts**. However, they are unique in their efficiency and high degree of specificity. Some more **important features of enzyme catalysis** are listed below.

### 1. Enzymes are the most efficient catalysts known

The enzyme catalyzed reactions proceed at fantastic high rates in comparison to those catalyzed by inorganic substances. Thus one molecule of an enzyme may transform one million molecules of the substrate (reactant) per minute. Like inorganic catalysis, enzymes function by lowering the activation energy of a reaction. For example, the activation energy of the decomposition of hydrogen peroxide without a catalyst is 18kcal/mole. With colloidal platinum (inorganic catalyst), the activation energy is lowered by 11.7 kcal/mole. The enzyme catalyze lowers the activation energy of the same reaction to less than 2 kcal/mole.

### 2. Enzyme catalysis is marked by absolute specificity

An enzyme as a rule catalysis just one reaction with a particular substance. For example, urease (an enzyme derived from soya bean) catalysis the hydrolysis of urea and no other amide, not even methyl urea.

### 3. The rate of enzyme-catalyzed reaction is maximum at the optimum temperature

The rate of enzyme catalyzed reaction is increased with the use of temperature but up to a certain point. There after the denatured as its protein attendance is gradually destroyed. Thus the rate of reaction eventually drops drop and eventually becomes zero when the enzyme is completely destroyed the rate of an enzyme reaction with raising of temperature gives a bell-shaped curve. The temperature at which the reaction rate is maximum is called as optimum temperature.

### 4. Rate of enzyme catalyzed reaction is maximum at the optimum pH

The rate of an enzyme-catalyzed reaction varies with pH of the system. The rate passes through a maximum at a particular pH, known as the optimum pH. The enzyme activity is lower at other values of pH. Thus many enzymes of the body function best at pH of about 7.4, the pH of the blood and body fluids.

### 5. Enzymes are markedly inhibited or poisoned

The catalytic **activity** of an enzyme is often reduced (inhibited) or complete **destroyed** (poisoned) by **addition of other substances**. These inhibitors or poisons interact with the active functional groups on the enzyme surface. For example, heavy metal ions ( $\text{Ag}^+$ ,  $\text{Hg}^+$ ) react with the  $-\text{SH}$  groups of the enzyme and poison it.

### 6. Catalytic activity of enzymes is greatly enhanced by the presence of Activators or Coenzymes

Activators are **metal ions**  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  etc., which got weakly bonded to enzyme molecules and **promote** their catalytic action. Thus it has been found that the addition of sodium chloride ( $\text{Na}^+$ ) makes amylose catalytically very active. Often, a small non-protein (vitamin) termed a coenzyme when present along with an enzymes, promotes the catalytic activity of the latter.

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**Strong Concepts + Smart Practice = Success**

**Best of Luck**